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GROUNDWATER MIXING ZONE GUIDELINE

I. Process for Use of the Natural Attenuation (Groundwater Mixing Zone) Alternative

This guideline describes the process required for establishing groundwater mixing zones, demonstration criteria required for pursuing the natural attenuation alternative and the use of groundwater models in groundwater mixing zone applications. The SCDHEC Guidance on Mixing Zone Applications (1995) was followed for preparation of this guideline.

Details

The State of South Carolina Water Classifications and Standards (R.61-68 and R.61-69) apply to all groundwater of the state. Active cleanup measures are required for contaminants at concentrations that exceed regulatory limits (State Primary Drinking Water Standards). R.61-68 allows for establishment of "groundwater mixing zones", where contaminants may exceed maximum contaminant levels (MCLs) if certain conditions are met. Groundwater mixing zones are areas down-gradient from a source of contamination where concentrations are decreasing as a result of contaminant degradation, volatilization and/or mixing with the natural waters of the formation.

Each proposed mixing zone requires unique hydrogeologic information and assessment, depending on the contaminants present and conditions at the site. Natural attenuation as a remedial option may lend itself to the types of contaminants and conditions that exist at SRS.

Conditions for Establishing Groundwater Mixing Zones

The conditions for establishment of a groundwater mixing zone include:

Reasonable measures have been taken or binding commitments made to minimize the addition of contaminants to groundwater and/or control the migration of contaminants in groundwater.

The groundwater in question is confined to a shallow geologic unit that has little or no potential of being an underground source of drinking water, and discharges or will discharge to surface waters without contravening the surface water standards set forth in R.61-68.

The contaminant(s) in question occur on the property of the applicant, and there is minimum possibility for groundwater withdrawals (present or future) to create drawdown such that contaminants would flow off-site.

The contaminants are not dangerously toxic, mobile or persistent.

The steps required for reviewing the conditions with respect to a specific site under consideration for a mixing zone application are:

<u>Step 1</u> – Determine the relative toxicity of the contaminants present in groundwater. If contaminants are especially toxic (e.g. dioxin), use of the natural attenuation alternative is not practical.

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- <u>Step 2</u> Determine the relative persistence and mobility of the contaminants in the aquifer(s). If the contaminants are long-lived (e.g. PCBs) or highly mobile in groundwater, use of the natural attenuation alternative is not practical.
- **Step 3** Determine which aquifer(s) are effected by existing contamination.
- <u>Step 4</u> Evaluate the source of the contamination and the likelihood for additional spreading of contaminant plume(s). Take into account source removal or mitigation (by capping, or through active or passive treatment, etc.), the type of contaminants (i.e., VOCs vs. metals or radioactive compounds), and the potential for additional contaminant transport.
- Step 5 Consider the likelihood of additional contamination of groundwater via transport of contaminant(s) through the soil column to groundwater. As part of this, consider vadose zone transport parameters; thickness of the vadose zone, vertical groundwater velocity, recharge rate, foc, cation exchange capacity, etc. Use of vadose zone transport models (e.g. MEPAS or SESOIL) or relevant equations may aid in this assessment.
- <u>Step 6</u> Determine the potential for future use of shallow groundwater aquifers as a source of drinking water.
- <u>Step 7</u> Review analytical data to ascertain that contamination is limited to shallow aquifers, and compare hydraulic head measurements in shallow and deep aquifers to assess vertical flow potential and possible flow across confining (or semi-confining units).
- <u>Step 8</u> Consult hydrostratigraphic maps and potentiometric maps to establish the relationship between flow in effected aquifer units/zones and surface water features. If aquifer(s) are discharging to surface water, compare contaminant concentrations from the well or CPT location nearest the discharge point to surface water standards (set forth in R.61-68).
- <u>Step 9</u> Check contaminant plume maps to ensure that contaminant plume(s) do not extend beyond SRS property boundaries or into adjacent operable unit(s). Assess the possibility of co-mingling contaminant plumes. If co-mingling plumes exist, the concentrations of contaminants entering the operable unit under study must be considered as part of the groundwater mixing zone application.
- <u>Step 10</u> Check for nearby production wells, and determine the potential effects of pumping on contaminant plume geometry.

If the four conditions for establishing a groundwater mixing zone are met, a case may be made for use of the natural attenuation remediation alternative. In order to accomplish this, a groundwater mixing zone application must be approved by DHEC.

<u>Demonstration Criteria for the Mixing Zone Application</u>

Per DHEC guidance, the following must be specifically addressed in the mixing zone application. Typically, most of these criteria are part of the RI/RFI document.

Demonstration that the source has been removed, remediated, and/or contained to minimize additional contamination of the aquifer and/or prevent exposure to any receptor (also part of the first condition).

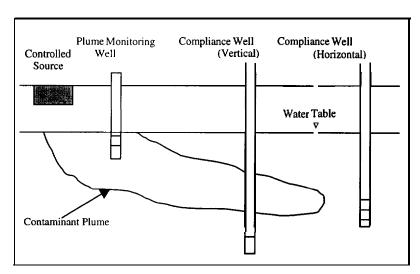
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Demonstration that contamination in groundwater has been completely characterized by establishing the types and concentrations of contaminants that exist at the site.

Definition of the horizontal/vertical extent of soil and/or groundwater contamination and plume movement.

Demonstration that contaminants will remain confined in a shallow geologic unit until discharge to surface water or attenuation to standards (MCLs) occurs. The contaminants must not migrate to a deeper aquifer. A cross sectional view of a compliance monitoring scenario to satisfy this is shown below:



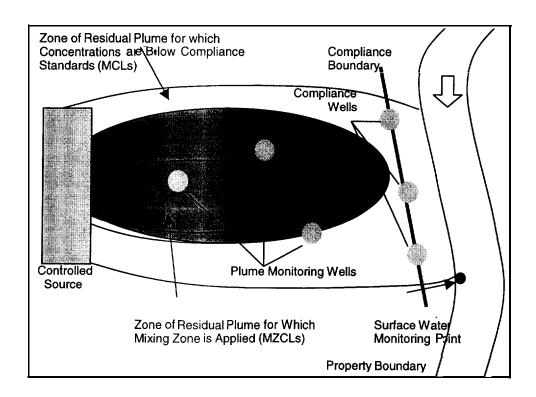
Compliance and Monitoring Well Scenario with Vertical (Depth), Horizontal (Downgradient) and Plume Monitoring

- 1. Demonstration that the area or volume of contamination that exceeds MCLs is not significantly increasing prior to discharge or attenuation.
- 2. Demonstration that contaminants (at concentrations above MCLs) will not extend beyond property boundaries or the established compliance boundary. This is accomplished by groundwater flow/fate and transport modeling or through other hydrogeologic evidence (including calculations).
- 3. Demonstration that potential receptors (e.g. through drinking water wells) have been identified.
- 4. Demonstration that there is no current use (and a minimum potential for future use) of effected groundwater as a source of drinking water for the anticipated duration of the mixing zone status period.
- 5. If groundwater discharges to surface water (on-site or at the property boundary), data must be obtained to identify the concentrations of contaminants and rate of discharge to the surface water body. Documentation of in-stream water quality standards (surface water monitoring) is required.
- 6. Site-specific mixing zone concentration limits (MZCLs) must be established for the site. MZCLs are the highest concentration for the specific contaminants identified at the site.

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Compliance Monitoring

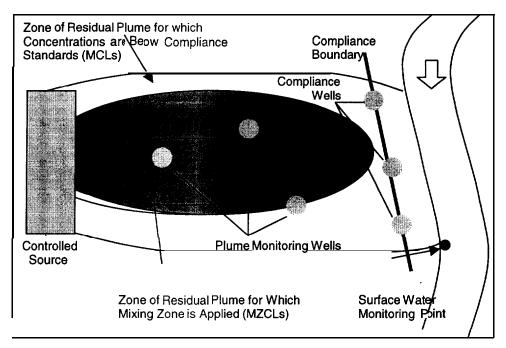
As part of the groundwater mixing zone application, a monitoring program must be proposed to show compliance with mixing zone requirements. The program must demonstrate compliance with; (1) MZCLs within the plume(s), and (2) MCLs at compliance boundaries. Compliance boundaries are required near the down-gradient plume boundary, at property boundaries, or surface discharge areas. The monitoring program will cont inue until MCLs within the plume are achieved. Mixing zone scenarios for compliance monitoring with and without surface water discharge are shown in the following diagrams:



Potential Mixing Zone Scenario with Plume Discharging to On-Site Stream

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Potential Mixing Zone Scenario with Plume Confined to Property

Use of Groundwater Modeling in Support of the Mixing Zone Application

Groundwater flow/contaminant transport models are useful for satisfying the requirements of groundwater mixing zone applications. Models may be used for the following:

- 1. Demonstrate site flow conditions and contaminant transport over time (horizontal and vertical migration).
- 2. Verify the time required for mixing zone status (exceeding regulatory status) and the area/volume effected.
- 3. Demonstrate that contaminants are highly unlikely to contaminate deeper aquifer zones (at concentrations greater than standards). Vertical movement must be especially well defined in potential recharge areas.
- 4. Demonstrate that migration of contaminants at concentrations above MCLs will not likely extend offsite. The demonstration must include the potential for groundwater use in the surrounding area (if this applies) that may result in contaminant flow offsite (for the time period the mixing zone will be in effect).
- 5. Identify appropriate down-gradient locations for compliance boundary wells.

The type of model selected (groundwater flow/contaminant transport) depends on the conditions at a particular site and the goals of modeling. Refer to the Groundwater Modeling Protocols for guidance in model selection, data evaluation and model design/application.

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Definitions

Analytical element method – a means of using the principle of superposition to combine the solutions to many analytical equations. Analytical functions representing stresses such as wells, line sinks and circular recharge areas and features, such as an impermeable barrier, are summed and expressed in terms of discharge potential.

Analytical model – a model that uses closed-form solutions to the governing equations applicable to groundwater flow and transport processes.

Application verification – using the set of parameter values and boundary conditions from a calibrated model to approximate acceptably a second set of field data measured under similar hydrologic conditions.

Boundary condition – a mathematical expression of a state of the physical system that constrains the equations of the mathematical model.

Calibrated model – a model for which all residuals between calibration targets and corresponding modeling outputs, or statistics computed from residuals, are less than pre-set acceptable values.

Calibration – the process of refining the model representation of the hydrogeologic framework, hydraulic properties and boundary conditions to achieve a desired degree or correspondence between the model simulations and observations of the groundwater flow system.

Calibration targets – measured, observed, calculated or estimated hydraulic heads or groundwater flow rates that a model must reproduce, at least approximately, to be considered calibrated. The calibration target includes the value of the head or flow rate and its associated error of measurement, so that undue effort is not expended attempting to get a model application to closely reproduce a value, which is known only to within an order of magnitude.

Code verification — software testing that includes comparison with analytical solutions and other similar codes to demonstrate that the code used represents its mathematical foundations.

Computer code – the assembly of numerical techniques, bookkeeping, and control language that represents the model from acceptance of input data and instructions to delivery of output.

Conceptual model – an interpretation or working description of the characteristics and dynamics of the physical system.

Converged Solution - the solution resulting from the iterative solution process.

Convergence Criterion - the amount of acceptable solved parameter differences between iteration solutions in the iterative solution process. This is typically a limiting parameter defined by the user in numeric groundwater models.

Darcy's Law - the basic equation of flow for groundwater systems. Flow velocity (rate) equals hydraulic conductivity times the gradient.

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Deterministic process – a process in which there is an exact mathematical relationship between the independent and dependent variables in the system.

Dirichlet condition - specified head boundaries for which head is given.

Domain - the area of a groundwater system being modeled.

Dupuit assumptions – assumptions applied to an unconfined aquifer; 1) flow lines are horizontal and equipotential lines are vertical, and 2) the horizontal hydraulic gradient is equal to the slope of the free surface and is invariant with depth.

Fidelity – the degree to which a model application is designed to resemble the physical hydrogeologic system.

Finite-difference method – a numerical technique for solving a system of equations using a rectangular mesh representing the aquifer and solving for the dependent variable in a piece-wise manner.

Finite-element method – a numerical technique for solving a system of equations using an irregular triangular or quadrilateral mesh representing the aquifer and solving for the dependent variable in a continuous manner.

Flow model - a groundwater model that solves for heads (and resultant flow directions and magnitudes).

Gradient - the measure of the head changes in a groundwater system. For an unconfined aquifer, the slope of the water table surface is essentially equal to gradient.

Grid - the collection of nodes in a numeric groundwater model.

Groundwater flow model – an application of a mathematical model to represent a site-specific groundwater flow system.

Hydraulic Head - the term used to represent the energy of the groundwater system at any particular point. Head is essentially equivalent to the water table in unconfined aquifers. Head is measured in length (height) units like feet or meters from a datum elevation (such as mean seal level).

Heterogeneity - a term indicating that a parameter changes spatially.

Homogeneity - a term indicating that a parameter does not change spatially.

Hydraulic conductivity - the measure of a porous media's ability to transmit water. Used in Darcy's Law as the proportionality constant between the gradient and flow velocity terms.

Hydrodynamic dispersion - the combined effects of molecular diffusion and mechanical dispersion. Also commonly just called dispersion.

Hydraulic properties – properties of soil and rock that govern the transmission (e.g., hydraulic conductivity, transmissivit y, and leakance) and storage (e.g. specific storage, storativity and specific yield) of water.

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Hydrostratigraphic units - units that are delineated based on hydrogeological as well as geological parameters.

Iterative solution - the process and result of finding an answer by using better and better approximate solutions. A technique commonly used in numeric groundwater models. Each cycle of the process is called an iteration.

Inverse method – a method of calibrating a groundwater flow model using a computer code to systematically vary inputs or input parameters to minimize residuals or residual statistics.

Mathematical model – mathematical equations expressing the physical system and including simplifying assumptions. The representation of a physical system by mathematical expressions from which the behavior of the system can be predicted.

Mechanical dispersion - a physical process that represents the mixing of solutes due to variations in flow velocities. These variations are due to three primary factors: (1) variations in pore sizes, (2) differences in path lengths, and (3) variations of velocities within each pore due to friction at the pore walls.

Method of characteristics (MOC) – a numerical method to solve solute transport equations by construction of an equivalent of ordinary differential equations using moving particles as reference points. Also known as the particle-in-cell method.

Model – an assembly of concepts in the form of mathematical equations that portray understanding of a natural phenomenon.

Molecular diffusion - a chemical process at the molecular level that causes areas of higher concentrations to want to equilibrate with areas of lower concentrations.

Nodes - the discrete points in numeric groundwater models where we solve for head.

Numerical methods – a set of procedures used to solve the equations of a mathematical model in which the applicable partial differential equations are replaced by a set of algebraic equations written in terms of discrete values of state variables at discrete points in space and time. Those in common use are the finite-difference method, finite-element method, boundary-element method and analytical element method.

Over-calibration – achieving artificially low residuals by inappropriately fine-tuning model parameters and not performing application verification.

Random walk — a method of tracking a large number of particles with the number of particles proportional to solute concentration, and each particle advected deterministically and dispersed probabilistically.

Residual – the difference between the computed and observed values of a variable at a specific time and location.

Sensitivity – the degree to which the model result is affected by changes in a selected model input representing hydrogeologic frame work, hydraulic properties and boundary conditions.

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Simulation – one complete execution of a groundwater modeling program, including input and output.

Sink – a process or a feature from which water is extracted from the groundwater flow system.

Steady-State - if a groundwater system does not change over time, then the system is in a steady-state condition. Also refers to the type of numeric modeling where results are not expected to change over time.

Stochastic - consideration of subsurface media and flow parameters as random variables.

Stochastic model – a model representing groundwater parameters as random variables.

Stochastic process – a process in which the dependent variable is random (so that prediction of its value depends on a set of underlying probabilities) and the outcome at any instant is not known with certainty.

Transient - if a groundwater system changes over time, then the system is in a transient condition. Also refers to the type of numeric modeling where the results reflect changes over time.

Transport model - a groundwater model that solves for concentrations of solutes.

Water balance - a process of equating the water inflows to a groundwater system with the water outflows, accounting for any changes in storage of water in the system.

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